

2-3-94

F-3 FEB 1994

Date Out:

Chemical Code: 032201

DP Barcode: D163796,
 D163800, D163808, D163811,
 D163812, D163815, D163818,
 D163821, D163823, D163824,
 D163826, D163829, D163830,
 D163832, D170496, D194416,
 and D198589

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: Lois Rossi, PM # 74
 Linda Propst, PM # 73
 Special Review and Reregistration Division (H7508W)

From: Paul Mastradone, Section Head *Paul J Mastradone*
 Chemistry Review Section 1
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Through: Henry Jacoby, Chief *Henry Jacoby 2/7/94*
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of diquat dibromide.

| | | | |
|---------------|---|-------------|------------------|
| Common Name: | Diquat | Trade name: | Diquat, Aquacide |
| Company Name: | Chevron Chemical Co., Richmond, CA | | |
| ID #: | 032201 | | |
| Purpose: | Review of studies for environmental fate data requirements in support of a reregistration eligibility document. | | |

| Type Product: | Action Code: | EFGWB #(s): | Review Time: |
|---|--------------|--|--------------|
| nonselective, contact herbicide and desiccant | 660 | 91-0544, 91-0546, 91-0547, 91-0548, 91-0549, 91-0551, 91-0545, 91-0550, 91-0554, 91-0555, 91-0556, 91-0557, 92-0134, 93-0985 | 43 days |



2074184

STATUS OF STUDIES IN THIS PACKAGE:

| Guideline # | MRID | Status |
|-------------|----------|--------|
| 161-3 | 40246101 | A |
| 162-1 | 40972301 | A |
| 163-1 | 40348601 | A |
| 163-1 | 40246801 | C |
| 164-1/164-5 | 42060301 | A |
| 164-1/164-5 | 42060302 | A |
| 164-2 | 40917403 | A |
| 164-5 | 40335201 | C |
| 165-4 | 40326901 | A |
| 165-5 | 40326904 | A |
| 165-5 | 40326903 | A |
| 165-5 | 40380701 | A |
| 165-5 | 40326902 | A |
| | | |
| | | |

STATUS OF DATA REQUIREMENTS ADDRESSED IN THIS PACKAGE:

| Guideline # | Status |
|-------------|--------|
| 161-3 | S |
| 162-1 | S |
| 163-1 | S |
| 164-1 | S |
| 164-2 | S |
| 164-5 | S |
| 165-4 | S |
| 165-5 | S |
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¹Study Status Codes: A=Acceptable, U=Upgradeable
C=Ancillary I=Invalid.

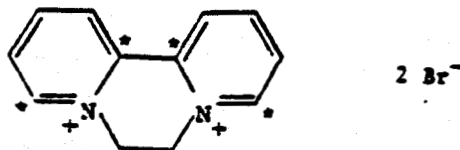
²Data Requirement Code S=Satisfied P=Partially satisfied
N=Not satisfied R=Reserved W=Waived.

Common name: Diquat

CAS number: 85-00-7

Chemical name: 1,1'-Ethylene-2,2'-bipyridylium ion, dibromide salt; 6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazdium ion, dibromide salt.

Structure:



Formulations: Soluble concentrate or pressurized liquid

Mode of action: Lipid peroxidation resulting in disruption of cell membrane

Physical/Chemical properties:

Molecular formula: $C_{12}H_{12}N_2Br_2$.

Molecular weight: 344.0.

Physical state: Crystalline.

Vapor pressure: <0.013 mPa.

Solubility at 20 C: 700 g/L in water; slightly soluble in alcohols and hydroxylic solvents, insoluble in non-polar organic solvents.

2. TEST MATERIAL:

Studies 1-3, 10-13: Active ingredient. Studies 6-8 and 14: Soluble concentrate. Study 5: Technical chemical. Study 4 and 9: Formulation not identified.

3. STUDY/ACTION TYPE:

Review of studies to fulfill environmental fate data requirements for: photodegradation on soil, aerobic soil metabolism, mobility (batch equilibrium), terrestrial field dissipation (short and long term), aquatic field dissipation, accumulation in fish, and accumulation in non-target aquatic organisms.

4. STUDY IDENTIFICATION:

1. Joseph, R.S.I., and M.W. Skidmore. 1987. Diquat: Photolytic stability on soil surfaces. Laboratory Project ID: RJ0573B. Unpublished study performed by ICI Plant Protection Division, Berkshire, UK, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40246101).
2. Johnston, J.J. 1988. Aerobic soil metabolism of diquat. Laboratory Project ID: MEF-0071. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40972301a).
Daly, D. 1988. Aerobic soil metabolism of ^{14}C -diquat. ABC Laboratory Project ID: Final Report No. 36558. Chevron Study No. MEF-0071. Unpublished study performed by Analytical Biochemistry Laboratories, Inc., Columbia, MO, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40982301b).
3. Pack, D.E. 1987. Freundlich soil adsorption coefficients of diquat. Laboratory Project ID No. MEF-0069/8716930. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40348601).
4. Pack, D.E. 1984. The lack of mobility of diquat in sandy soil - laboratory study. Laboratory project ID No. 722.2. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40246801).
5. Riley, D. 1986. Diquat: Leaching and adsorption/desorption in soil. (Comments on EPA diquat registration standard dated June 1986). Unpublished study performed by ICI, Berkshire, England, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40348602).
Riley, D. and R.P. Gratton. 1974. Unavailability to plants of diquat residues in soils. Transactions of the 30th International Congress of Soil Science. Volume III: 193-202. (MRID 40348608).

- Hebden, J.M.C. and D. Riley. Paraquat and diquat: Bioassay with wheat seedlings and its application for determining the strong adsorption capacities (SAC-WB) of soils. Unpublished study performed by ICI, Berkshire, England, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40348609).
6. Fujie, G.H. 1991. Diquat cation soil dissipation study on potatoes in New York. [supplemental to: Diquat cation soil dissipation study on potatoes in New York (interim report) MRID 40917404.] Laboratory Project ID: R010/7059SOILF. Unpublished study performed by A&S Environmental Testing, Inc., Reading, PA, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 42060301).
- Fujie, G.H. 1988. Diquat cation soil dissipation study on potatoes in New York (interim report). Laboratory Project ID: R010/7059SOIL. Unpublished study performed by A&S Environmental Testing, Inc., Reading, PA, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40917404).
- Hamada, A.L., J. Jiminez, and G.H. Fujie. 1987. Method validation report. Determination of diquat residues in soil by gas chromatography method RM-5G-1. Laboratory Project ID: RM-5G-1. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40335202).
7. Fujie, G.H. 1991. Diquat cation soil dissipation study on potatoes in Idaho. [supplemental to: Diquat cation soil dissipation study on potatoes in Idaho (interim report) MRID 40917405.] Laboratory Project ID: R010/7060SOILF. Unpublished study performed by A&S Environmental Testing, Inc., Reading, PA, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 42060302).
- Fujie, G.H. 1988. Diquat cation soil dissipation study on potatoes in Idaho (interim report). Laboratory Project ID: R010/7060SOIL. Unpublished study performed by A & S Environmental Testing, Inc., Reading, PA, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40917405).
8. Fujie, G.H. 1988. Aquatic field dissipation studies with diquat herbicide. Laboratory Project ID: R10/1642AQDISS. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40917403).
 9. Cole, J.F.H., I. Laws, J.E.B. Stevens, D. Riley, and W. Wilkinson. 1986. Long-term high-rate trial, Frensham, U.K., crop and soil data for the period 8-14 years after treatment. Laboratory Project ID: RJ0481B. Unpublished study performed by ICI, Plant Protection Division, Berkshire, UK, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40335201).
 10. Hammer, M.J., E. Farley, and I.R. Hill. Diquat: Investigation of accumulation in bluegill sunfish in a flow-through system. Laboratory Project ID: RJ0608B. Unpublished study performed by Imperial Chemical Industries, PLC, Berkshire, England, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40326901).
 11. Hammer, M.J., E. Farley and I.R. Hill. 1987c. Diquat: Investigation of accumulation in Daphnia magna in a flow-through system. Laboratory Project ID RJ0584B. Unpublished study performed by Imperial Chemical Industries, PLC, Bracknell, Berkshire, ENG, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40326903).
 12. Hammer, M.J., E. Farrelly, and I.R. Hill. 1987a. Diquat: Investigation of accumulation and elimination in mayfly nymph, Cloen dipterum, in a flow-through system. Laboratory Project ID No. R J 0609 B. Unpublished study performed by ICI Plant Protection Division, Bracknell, Berkshire ENG, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40380701).
 13. Thompson, R.S. 1987. Diquat: Determination of bioconcentration by Pacific

oysters (*Crassostrea gigas*). Laboratory Project ID BL/B/3092. Unpublished study performed by Imperial Chemical Industries, PLC, Devon, ENG, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40326902).

- 14 Fujie, G.H. 1987b. Accumulation of diquat in aquatic non-target organisms (interim report). Laboratory Project Identification R-101655INT. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40326904).

Fujie, G.H. 1987a. Accumulation of diquat in aquatic non-target organisms. Laboratory Project Identification R10/1655FISH. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40458301).

5. REVIEWED BY:
Laura Parsons
Agronomist, Review Section #1
EFGWB/EFED/OPP

Signature: Laura Parsons

Date: - 3 FEB 1994

6. APPROVED BY:
Paul Mastradone
Chief, Review Section #1
EFGWB/EFED/OPP

Signature: Paul J. Mastradone

Date: - 3 FEB 1994

7. CONCLUSION:

7.1. Data Requirement Status:

EFGWB considers the environmental fate data base for diquat to be complete for reregistration of diquat.

7.2. The following acceptable studies were reviewed in this package:

Photodegradation on Soil: 161-3

[¹⁴C]Diquat did not photodegrade on loam soil irradiated with a xenon arc lamp at 20.5-29.1 C for 107.42 hours (equivalent to approximately 32 days of natural sunlight). Diquat was the only compound identified in the extracts.

Aerobic soil metabolism: 162-1

Diquat at approximately 3 ug/g did not degrade in an aerobic sandy loam soil incubated at 25 C in the dark for 9 months.

Mobility -- Adsorption/Desorption: 163-1

Diquat is immobile with Freundlich K_{ads} values of 15 in sand sediment, 36-42 in two sand soils, and Freundlich K_{ads} values of 1882-10740 in sandy loam, sandy clay loam, and loam soils.

Dissipation -- Terrestrial field: 164-1; and Long-term field: 164-5

Diquat did not degrade for 3 years after application to two plots in New York; concentrations of diquat ion ranged from 0.01 to 0.32 ppm in the upper 15-cm soil depth. The two plots were planted to potatoes; the potato

vegetation from the clay loam soil plot was removed prior to application to represent bare ground application, the other plot was on a loam soil and diquat was sprayed on the vegetation. There were two applications of diquat dibromide (2 lb ai/gal SC/L) at 0.25 lb diquat ion/A/application (total 0.5 lb ai/A). In general, there was no pattern of leaching; diquat was recovered at 0.01-0.03 ppm from individual soil cores from the 15- to 22.5-cm soil depth.

Diquat did not degrade for 3 years after application to two plots of loam soil in Idaho; concentrations of diquat ion ranged from 0.01 to 0.13 ppm in the upper 35-cm soil depth. Application was made to bare ground and to potato vegetation. The plots were cultivated to 35 cm and in subsequent years cropped to a rotation of sugarbeets, wheat and potatoes. There were two applications of diquat dibromide (2 lb ai/gal SC/L) at 0.25 lb diquat ion/A/application (total 0.5 lb ai/A). There were no residues recovered from below 35 cm.

Field Dissipation - Aquatic and Aquatic Impact: 164-2

Diquat dissipated with half-lives of 1-2 days from Florida pondwater that was treated four times at 4 lb ai/A/application at approximately monthly intervals with diquat dibromide (Ortho Diquat Herbicide-HA). Diquat was removed from the water column by adsorbing to sediment and organic matter. The diquat concentrations in the sediment were variable ranging to a maximum of 1.2 ppm in the 0- to 5-cm depth with no discernible pattern of decline. In the aquatic dissipation study, the sites chosen were both near Gainesville, FL. Although the pond sites were treated under the same climatic conditions, the sediments were of different textures; one was sandy clay loam and the other was a sand sediment. The findings from these two sites were in agreement with findings from field dissipation studies conducted under a variety of climatic conditions and also were comparable to predictions from laboratory results.

Laboratory Accumulation - Fish: 165-4

Diquat residues did not significantly accumulate in bluegill sunfish exposed to [¹⁴C]diquat dibromide at approximately 1030 ppb diquat ion for 14 days under flow-through conditions. The maximum mean bioconcentration factors were 0.7X for edible tissues (muscle, skin, skeleton), 2.5X for nonedible tissues (viscera) and 1.03X for whole fish. Depuration was rapid, with approximately 50% of the accumulated [¹⁴C]residues eliminated from the fish tissues by day 3 of the depuration period.

Laboratory Accumulation - Non-target organisms: 165-5

Diquat residues did not significantly accumulate in Daphnia magna exposed to diquat dibromide at 10 ug/L in a laboratory flow-through system. The reported maximum bioconcentration factor was 8.3X, at 1 day post-exposure.

Diquat residues did not significantly accumulate in mayfly nymphs exposed to diquat dibromide at 1 mg/L in a laboratory flow-through system. The reported maximum bioconcentration factor was 32X, at 1 day post-exposure.

Diquat residues did not significantly accumulate in the soft tissue of Pacific oysters which were exposed to diquat dibromide monohydrate at 0.1 mg/L in a laboratory flow-through system for up to 28 days. The soft tissue bioconcentration factor for organisms exposed for 14 days was 5.5X;

for those exposed for 28 days, the soft tissue bioconcentration factor was 10.5X.

Field Accumulation - Non-target organisms: 165-5

Diquat did not significantly accumulate in tissues of tilapia and catfish from two fish ponds in Florida which were treated with diquat dibromide in four monthly applications at 4 lb diquat ion/A/application (total 16 lb diquat ion/A). Each application was equivalent to 0.36 ug diquat ion/mL. In tilapia, maximum concentrations of diquat ion were 8.5 and 0.30 ppm in nonedible (head, tail, and viscera) and edible (fillet plus skin) tissues, respectively. In catfish, the maximum concentrations of diquat ion were 0.06 and 0.15 ppm in edible (fillet) and nonedible (head, skin, tail, and viscera) tissues, respectively. Diquat ion concentrations in fish tissues did not increase with repeated applications. Diquat ion dissipated from the pond water with half-lives of 0.72-2.3 days.

The following four studies were submitted with this data package, but had been previously reviewed and found to be acceptable (12-pointer 2-21-89):

- Tegala, B., and M.W. Skidmore. 1987. Diquat: An aqueous photolysis study. Laboratory project ID: RJ 0613B. Unpublished study performed by ICI Plant Protection Division, Berkshire, UK, and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40418801; DP Barcode D163800).
- Johnston, J.J. 1988. Anaerobic aquatic metabolism of diquat. Laboratory Project ID: MEF-0072. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40972302; DP Barcode D163812).
- Johnston, J.J. 1988. Aerobic aquatic metabolism of diquat. Laboratory Project ID: MEF-0073. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40927601; DP Barcode D163815).
- Pack, D.E. 1987. Diquat volatility - laboratory study. Laboratory Project ID: MEF-0045/8709311. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (MRID 40245101; DP Barcode D163824).

7.5. Environmental Fate Assessment:

The primary route of environmental dissipation of diquat is adsorption to soil particles. Diquat does not hydrolyse, does not photodegrade in aqueous solutions, and is resistant to microbial degradation under aerobic and anaerobic conditions. There is essentially no microbial degradation of diquat in aerobic/anaerobic soil and aerobic/anaerobic aquatic systems.

In laboratory batch equilibrium studies, diquat was shown to be immobile with Freundlich K_{ads} values of 15-42 in sand sediment and two sand soils and Freundlich K_{ads} values of 1882-10740 in sandy loam, sandy clay loam, and loam soils. Diquat binds strongly to clay particles and indirect evidence

such as sorption to glassware would indicate adsorption to silt and sand particles as well; there was no clear correlation between soil organic matter content and adsorption. In field dissipation studies, diquat did not leach below the plow layer. Diquat is not volatile.

Diquat is used as an aquatic herbicide. When sprayed on the surface of ponds in an aquatic dissipation study conducted in Florida, diquat mixed quickly both laterally and by depth in the water column. Diquat was removed from the water column with a half-life of ≤ 2 weeks and was mostly bound to the upper 0-5 cm of the sediment layer; small amounts of diquat were recovered from the 5-10 cm sediment layer.

In short- and long-term field dissipation studies, diquat residues were extractable only by acid reflux and were shown to be persistent, but due to the apparent adsorption strength of diquat for soil clays, these bound residues do not appear to be available under environmental conditions.

Diquat is very persistent but is unlikely to be a groundwater contaminant due to its strong soil adsorptive properties. When applied to surface water systems diquat will most likely be associated with the sediment.

Diquat did not significantly accumulate in fish with bioconcentration factors of $\leq 2.5X$ with rapid depuration once fish are in pesticide-free water. In laboratory flow-through systems, diquat also did not significantly accumulate in *Daphnia*, mayfly nymphs, and oysters with maximum bioconcentration factors of $32X$; depuration was rapid in all organisms.

Diquat was recovered from non-edible tissues at up to 8.5 ppm in tilapia and up to 0.15 ppm in catfish which were incubated in cages in the Florida fish ponds used in the aquatic field dissipation study when the surface of a portion of the pond was treated with diquat. Diquat concentrations in the fish did not increase with repeated application of herbicide to the pond and diquat in the edible tissues decreased to ≤ 0.01 ppm by 14 days after application.

8. RECOMMENDATIONS:

The registrant should be informed of the following:

- a. The following study was not reviewed because it contains summary data only. Photochemical degradation of diquat. (TRID No. 460028002).
- b. The following study was not reviewed because the cover page and title page do not coincide with the remainder of this study. The text of this study is a duplicate to Study 2, MRID 40246101.

Riley, D. 1986. Diquat: Leaching and adsorption/desorption.
Laboratory Project ID: M4354B/8613585. Unpublished study performed

c. The status of the environmental fate data requirements for diquat are as follows:

| DATA REQUIREMENT | STATUS | MRID NUMBER |
|---|--------------------|--|
| 161-1 Hydrolysis | Fulfilled | |
| 161-2 Photodegradation in water | Fulfilled | 40418801 |
| 161-3 Photodegradation on soil | Fulfilled | 40246101 |
| 162-1 Aerobic soil metabolism | Fulfilled | 40972301 |
| 162-2 Anaerobic soil metabolism | Satisfied by 162-3 | |
| 162-3 Anaerobic aquatic metabolism | Fulfilled | 40972302 |
| 162-4 Aerobic aquatic metabolism | Fulfilled | 40927601 |
| 163-1 Mobility leaching | Fulfilled | 40348601 |
| 163-2 Laboratory volatility | Fulfilled | 40245101 |
| 163-3 Field volatility | Not required | -- |
| 164-1 Terrestrial field dissipation: soil | Fulfilled | 42060301 42060302 |
| 164-2 Terrestrial dissipation: aquatic (sediment) | Fulfilled | 40917403 |
| 164-3 Terrestrial dissipation: forestry | Not required | -- |
| 164-5 Terrestrial field dissipation: long-term soil | Fulfilled | 40335201 see 164-1 |
| 165-4 Accumulation in fish | Fulfilled | 40326901 |
| 165-4 Accumulation in non-target organisms | Fulfilled | 40326903 40326902 40326904 40380701 |

by Imperial Chemicals Industries, Berkshire, England, and submitted by Chevron Chemical Company, Richmond, CA. (41086001).

- c. The following three field dissipation studies were performed by Craven Laboratories and therefore cannot be submitted to fulfill Subdivision N data requirements:

MRID 40917406: Fujie, G.H. 1988. Diquat cation soil dissipation study on soybeans in Iowa (interim report). Laboratory Project ID: R010/7057SOIL. Unpublished study performed by Craven Laboratories, Inc., Austin, TX, and submitted by Chevron Chemical Company, Richmond, CA.

MRID 40917407: Fujie, G.H. 1988. Diquat cation soil dissipation study on soybeans in Florida (interim report). Laboratory Project ID: R010/7056SOIL. Unpublished study performed by Craven Laboratories, Inc., Austin, TX, and submitted by Chevron Chemical Company, Richmond, CA.

MRID 40917408: Fujie, G.H. 1988. Diquat cation soil dissipation study on sorghum in California (interim Report). Laboratory Project ID: R010/7058SOIL. Unpublished study performed by Craven Laboratories, Inc., Austin, TX, and submitted by Chevron Chemical Company, Richmond, CA.

9. BACKGROUND: Diquat dibromide is used as a nonselective contact herbicide for noncrop weed control, aquatic weed control, and a plant regulator and desiccant for agricultural seed crops. Terrestrial application rates range from 0.25 to 1.0 lb ai/A; aquatic rates range from 0.8 to 15 lb ai/A. Diquat dibromide may be formulated with paraquat and simazine. Single active ingredient formulations consist of 0.08-2 lb/gal and 0.19-2.36% SC/L, and 0.094-0.23% RTU. Diquat dibromide may be applied as a broadcast preharvest desiccant, foliar spray, directed spray, spot treatment, shoreline treatment, or water treatment and may be applied by aircraft. The use of a non-ionic surfactant is recommended. Do not graze treated areas or feed treated forage to livestock. Do not use seed from treated plants for food, feed, or oil purposes. For aquatic sites, do not use the treated areas for animal consumption, swimming, spraying, irrigation or domestic purposes for 14 days after treatment.

10 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Refer to attached reviews.

11 COMPLETION OF ONE-LINER:

12 CBI APPENDIX:

All data reviewed here are considered "company confidential" by the registrant and must be treated as such.

